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(21) International Application Number: PCT/US97/23509 (22) International Filing Date: 23 December 1997 (23.12.97) (30) Priority Data: 08/832,934 4 April 1997 (04.04.97) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: BUTLER, Terri, L.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). BRETSCHER, Kathryn, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). BERENS, Mark, C.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). BAKER, James, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LEHMAN, Gaye, K.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LEONARD, William, K.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CONTINUOUS FLUID-COATING FLOW CHEMICAL ALTERATION PROCESS (57) Abstract <p>A method for chemically altering the composition of a first coating fluid in continuous flow from a dispenser to a final substrate is disclosed. The method employs the steps of dispensing the fluid in a continuous flow from a source location into a second fluid, and imposing at least one condition on the first fluid to alter the chemical composition of the first fluid before that first fluid leaves the second fluid and contacts the final substrate.</p>		

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CONTINUOUS FLUID-COATING FLOW CHEMICAL ALTERATION PROCESS

Field of Invention

This invention concerns the use of a process that permits chemical
5 alteration of a fluid during continuous flow of that fluid to a final substrate.

Background of Invention

Multiple types of coating processes provide a means for delivering a
fluid, particularly a liquid, from a dispenser to a final substrate. Once the fluid has
10 arrived on the final substrate, the fluid can be altered physically or chemically.

Examples of fluid alteration after arrival at the final substrate
include continuous polymerization processes, evaporation of solvents, and the like.

PCT Patent Publication WO 0 031 725 discloses a process for
producing an ultra thin solid membrane for gas separation. U.S. Pat. No 4,132,824
15 discloses a method for casting ultra thin methylpentene polymer membranes.
Japanese Patent Specification JP HEI 2(1990) - 207870 discloses production of an
ultra thin film laminate.

U.S. Pat. No. 5,067,797 discloses a process for casting liquid
crystalline polymer solution on a bath. Japanese Patent Specification JP
20 83,035,723 discloses a composite porous and non-porous membrane manufacture
by pouring polymer solution onto a water surface, rolling, and winding non-porous
membrane obtained onto porous membrane.

U.S. Pat. No. 5,324,359 discloses a process for depositing droplets
and optionally dosing the droplets with radiation as they fall to a substrate.

25 World Patent No. 96/23595 (Melancon et al.) discloses a process for
coating a two-layer curtain, also known as a carrier fluid process, that uses a carrier
layer of fluid (such as water) to transport a functional layer (such as silicone or
other polymeric material) to a web. The advantage of this process is that it can be
used to generate very thin coatings (i.e. less than 1000 Å) without solvent dilution.

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Summary of Invention

The art of coating processes has not recognized either the possibility or the value in providing an opportunity for chemical reaction of a fluid during delivery in a continuous flow from a dispenser to a final substrate.

5 One aspect of the present invention is a method for chemically altering the composition of a first fluid in continuous flow from a dispenser to a final substrate, comprising the steps of dispensing the fluid in a continuous flow from a source location into a second fluid, and imposing at least one condition on the first fluid to alter the chemical composition of the first fluid before that first
10 fluid leaves the second fluid and contacts the final substrate during a coating or extrusion process.

 The first fluid can be a liquid, a gas, a combination of liquid and a gas, a combination of two or more gases, a combination of two or more liquids, a supercritical fluid, a combination of a supercritical fluid and a gas, a combination
15 of a supercritical fluid and a liquid, or a combination of two or more supercritical fluids.

 The second fluid can be a liquid, a gas, a combination of liquid and a gas, a combination of two or more gases, or a combination of two or more liquids as a mixture or as a multilayer, a supercritical fluid, a combination of a
20 supercritical fluid and a gas, a combination of a supercritical fluid and a liquid, or a combination of two or more supercritical fluids.

 The final substrate can be a solid, at least one liquid on a solid, or at least one gas on a liquid.

 The condition can be imposition of a single type of actinic radiation,
25 more than one type of actinic radiation imposed concurrently, or more than one type of actinic radiation imposed sequentially.

 Another condition can be adsorption of a reactive gas into the first fluid.

 Another condition can be transfer of heat to the first fluid by
30 conduction or radiation.

Another condition can be capture of activating particles or catalysts by the first fluid.

Another condition can be capture into the first fluid droplets from an activating fog.

5 Another condition can be imposition of an electric discharge.

Another condition can be imposition of an alternating or direct current of electric energy.

Another condition can be imposition of corona fields.

Another condition can be imposition of electric fields.

10 Another condition can be imposition of magnetic fields.

Another condition can be imposition of oscillating fields.

Another condition can be imposition of sound waves.

Another condition can be imposition of ultrasound.

Another condition can be imposition of shock waves.

15 Another condition can be imposition of pressure waves.

The dispenser can be an extrusion die, a nozzle, slide die, or other orifice from a source of the first fluid.

20 A feature of the present invention is the ability to alter chemical properties of a fluid between the time of its dispensing and the delivery to a final substrate.

Another feature of the invention is the ability to alter chemical properties in more than one manner from the time of dispensing to delivery.

25 An advantage of the present invention is the formation of a different chemical composition of a fluid on a final substrate from the time that the fluid is ejected from its source.

Another advantage of the present invention is that the second fluid can be inert to, i.e., substantially insoluble in, the first fluid or interactive with the first fluid such that the first fluid is chemically altered during the time of flight through the second fluid and before the first fluid contacts any solid.

Another advantage of the present invention is the first fluid can operate within the principles of gravitational flow during imposition of the conditions that changes the chemical composition of that first fluid.

Other features and advantages will become apparent with a more
5 detailed explanation of the embodiments of the invention.

Embodiments of the Invention

Coating and Extrusion Methods

Any coating and extrusion technique that relies on the transfer of a
10 fluid from a source to a final substrate is suitable for use with the present invention. Nonlimiting examples of coating techniques are generally found in the technical literature within treatises such as any of the "Coating Processes" and "Coatings" articles in Kirk-Othmer, Encyclopedia of Chemical Technology, Third and Fourth Editions (Wiley-Interscience, 1979 and 1994, respectively).

15 Of conventional coating methods, a number of coating techniques are desirable because of their ability to rely on the delivery of a fluid, particular one or more liquids, in precisely measured continuous fluid flows. Nonlimiting examples of these coating techniques are curtain coating, slide coating, extrusion die coating, and roll coating which are more completely described in Cohen and
20 Gutoff (Modern Coating and Drying Technology, VCH Publishers, 1992) and in Satas, (Coatings Technology Handbook, Marcel Dekker, Inc. 1991). Additional preferred methods of coating include carrier fluid coating which is more completely described in International PCT Patent Publication No. WO 96/23595 (Melancon et al.).

25 Melancon et al. discloses a process for coating a two-layer curtain, also known as a carrier fluid process, that uses a carrier layer of fluid (such as water) to transport a functional layer (such as silicone or other polymeric material) to a web. The advantage of this process is that it can be used to generate very thin coatings (i.e. less than 1000 Å) without solvent dilution.

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First Fluid

The first fluid can be a liquid, a gas, a combination of liquid and a gas, a combination of two or more gases, or a combination of two or more liquids either mixed or as a multilayer, a molten polymer, molten salts, liquid metals, or supercritical fluids contained in one or more sources and dispensed either
5 concurrently or sequentially in order to undergo a chemical alteration while in continuous flow prior to reaching a final substrate.

Any one or more of the fluids can be destined for the final substrate or can be discarded during the delivery of at least one of the other fluids to the final substrate. These discarded fluids are also known as carrier fluids, such as
10 described in Melancon et al. above.

Nonlimiting examples of first fluids that can be used as carrier fluids include water, hydrophilic liquids, hydrophobic liquids, noble gases, inert gases, and air which are otherwise nonreactive to the condition(s) between dispensing and delivery of the first fluid through the second fluid to the final
15 substrate.

The composition of the first fluid intended to undergo chemical reaction is otherwise known as the functional fluid. Nonlimiting examples of functional fluids include monomers, oligomers, pre-polymers, polymers, crosslinking agents, initiators, modifiers, and any other chemical that can exist in
20 fluid form at a single environment of a given temperature, a given pressure, and a given volume and is chemically reactive under any condition imposed during transport of that fluid in continuous flow through a second fluid.

Preferred examples of such fluids are liquid pre-polymers that are apt to undergo increased polymerization during transport through ambient air with
25 exposure to actinic radiation. Nonlimiting examples of such pre-polymers are silicone pre-polymers either in neat or in solvent, either dispensed alone or with a carrier fluid.

Functional fluids may be miscible or immiscible with the carrier fluid.

30 Preferred functional layer formulations include silicone-urea release formulations (as disclosed in U.S. Pat. No. 5,045,391 (Brandt et al.)); and silicone or

fluorosilicone polymers (such as ethylenically unsaturated-, hydroxy-, epoxy-terminated or pendant functional silicone and fluorosilicone pre-polymers); or other release polymers with suitable low surface energy (such as poly(organosiloxanes), fluoropolymers, and the like) as disclosed in PCT publication WO97/12282 as well as polymers useful for adhesives including but not limited to acrylates, silicone ureas, and methacrylates. The mole percent of crosslinkable groups is preferably 0 to 20 mole%, more preferably 0 - 15 mole%, and most preferably 0 - 10 mole%. For addition cure systems, both vinyl and alkenyl (number of carbons greater than 2 and less than 10) crosslinking groups may be used. The distribution of crosslinks may be unimodal or multimodal, as in the presence of higher molecular weight silicone gums and silicate resins as additives. More preferably, functional layers are selected from the group consisting of prepolymers with terminal and/or pendant crosslinking functionalities including, but not limited to silicone pre-polymers, silicone-urea polymers, acrylate functional polymers, and epoxy functional polymers and fluoropolymers disclosed above.

Preferably the silicone, fluorosilicone and fluoropolymer functional layer pre-polymers have a number average molecular weight ranging from 2,000 - 60,000 Da and 1 - 30,000 mPas, i.e. suitable for solventless coating. Additionally, solvent can be used to dissolve higher molecular weight silicone and fluorosilicone pre-polymers. More preferably, the functional layer pre-polymers have number average molecular weights of 10,000 - 30,000 Da with viscosities of 200 - 20,000 mPas.

For addition cure silicone pre-polymers, a nonlimiting list of silyl hydride crosslinkers include Dow Corning as homopolymers (Syl-Off™ 7048), copolymers (Syl-Off™ 7678) and mixtures (Syl-Off™ 7488) used in the amounts corresponding to 1:1 to 10:1 silyl hydride:vinyl ratio. For 100% solids coating, an appropriate amount of an inhibitor can be used to achieve good cure and an adequate pot life. A non-limiting example of an inhibitor is a 70:30 ratio of fumarate in benzyl alcohol to achieve good cure and adequate pot life. For solvent based coating, an inhibitor may not be needed for low percent solids dispersions.

For addition cure silicone functional layer polymers, both thermal and ultraviolet ("UV") initiated platinum catalysts can be used in the first fluid. Nonlimiting examples of platinum thermal catalysts are Dow Corning (Midland, MI) Syl-Off 4000 and Gelest (Tullytown, PA) platinum-

5 divinyltetramethyldisiloxane complex (SIP6830.0 and SIP6831.0). A nonlimiting example of a platinum UV catalyst is disclosed in U.S. Pat. No. 4,510,094 (Drahnak). Unlike the thermal catalyst, the UV catalyst does not require an additional inhibitor since the complex is effectively inhibited until exposure to UV.

Chemical additives or modifiers can be added to the functional layer composition. These chemical additives may include higher molecular weight
10 gums, silicate resins, surface active agents, particulate fillers, etc.

Nonlimiting examples of silicone gums include vinyl functional gums ranging in number average molecular weights from 60,000 to 800,000 Da available from Gelest (DMS-41, DMS-46, DMS-52) and ethylenically unsaturated
15 organopolysiloxane gums prepared according to U.S. Pat. No. 5,468,815 and 5,520,978 (Boardman) and in European Patent Publication 0 559 575 A1.

Preferably, the alkenyl-functional silicones had 2 to 10 carbon atoms with a molecular weight of approximately 440,000 Da. When silicone gums were used as additives to low viscosity silicone pre-polymers in 100% solids formulations, their
20 molecular weight was preferably less than 800,000 Da, more preferably less than 600,000 Da, and most preferably less than 500,000 Da. Their concentration was preferably less than 20% (w/w) in the silicone pre-polymer, more preferably less than 10% (w/w) and most preferably less than 5% w/w.

A non-limiting list of silicate resins include Syl-Off (Dow Corning)
25 7615, Gelest vinyl Q resin VQM-135 and VQM-146 which are provided as dispersions of silicate in silicone. Preferably, the silicate resin is present at 5 to 100% w/w in the silicone pre-polymer, more preferably 0 to 75%, most preferably 0 to 50% (w/w).

A nonlimiting list of surface active agents include low molecular
30 weight acrylate based surfactants such as Modaflow (Monsanto, St. Louis, MO) and BYK-358 (BYK-Chemie, Owens Hill, MD), silicone surfactants such as

Silwet™ (OSI, Danbury, CT), and fluorochemical surfactants such as Fluorads (3M, St. Paul, MN) and Zonyl (Dupont, Willimington, DE) leveling agents.

While the first fluid requires at least one gas or at least one liquid, optionally, one can also include particulate solids therein if not disruptive to any of dispensing, transport, or delivery of the first fluid. A nonlimiting list of particulate fillers include hydrophobic fumed silica such as CAB-O-SIL™ TS-530, TS-5610, and TS-720 (both from Cabot Corp. of Billerica, MA) and AER-O-SIL™ R812, R812S, R972, R202 (from Degussa Corp. of Ridgefield Park, NJ). The preferred inorganic particles include fumed, precipitated or finely divided silicas. A non-limiting list of low surface energy fillers includes hydrophobically treated fumed silica, polymethylmethacrylate beads, polystyrene beads, silicone rubber particles, teflon particles, and acrylic particles. Other particulate fillers which can be used but which are of higher surface energy include but are not limited to silica (not hydrophobically modified), titanium dioxide, zinc oxide, iron oxide, alumina, vanadium pentoxide, indium oxide, tin oxide, and antimony doped tin oxide. High surface energy particles that have been treated to lower the surface energy are also useful.

More preferred inorganic particles include colloidal silicas known under the tradenames of CAB-O-SIL™ (available from Cabot) and AEROSIL™ (available from Degussa). CAB-O-SIL™ TS-530 is a high purity fumed silica which has been treated with hexamethyldisilazane (HMDZ). CAB-O-SIL™ TS-610 is a high purity fumed silica treated with dichlorodimethyl silane. The treatment replaces many of the hydroxyl groups on the fumed silica with trimethylsilyl groups. CAB-O-SIL™ TS-720 is a high purity fumed silica which has been treated with a dimethyl silicone fluid. As a result the silica is a low surface energy particle.

Most preferably the filler is a hydrophobically modified fumed silica treated in situ with HMDZ to chemically bind the silica to the pre-polymer, available from Nusil Corporation (Carpinteria, CA). The composition of the hydrophobic filler is preferably 0.1 to 20%, more preferably 0.5 to 10% most preferably 1 to 5% w/w.

mRads per unit exposed area, ranging from about 1 mRad/cm² to about 1000 mRad/cm² in the case of other types of radiation.

The source of actinic radiation can be any locus or combination of loci that generates radiation of the particular wavelength(s) desired, ranging from the sun to "black lights" to medium pressure mercury lamps to cobalt radiation sources, all known to those skilled in the art for providing energy for chemical reaction of a fluid on a solid or in another liquid.

The amount of radiation dosage depends on the amount of chemical reaction desired for the first fluid while in transport from the dispenser through the second fluid to the final substrate. Nonlimiting examples of amounts of chemical reaction include full polymerization of the pre-polymer before it reaches the final substrate; partial polymerization of the pre-polymer that provides "green strength," useful rheological properties, or other temporary handling advantages between dispensing of the first fluid as a liquid and delivery of the pre-polymer to the final substrate for further processing; or some combination of types of chemical reaction either operating concurrently or sequentially before the first fluid reaches the final substrate.

For example, a staged chemical reaction of two liquid monomers emerging from a dispenser can form a pre-polymer followed by merging of that first fluid with a flow of crosslinking agent that then completes the polymerization before the first fluid reaches the final substrate. Depending on the size and shape of the dispenser, one can generate a first fluid in continuous flow that forms a string, a sheet, or some other three-dimensional object as a first fluid in the second fluid. By the completion of flight through the second fluid, the condition(s) imposed on that fluid have chemically transformed that object into a solid for landing on the final substrate.

Final Substrate

The final substrate can be merely a landing spot for the chemically altered first fluid or can be a major surface of a final product that is improved by the coating of the chemically altered first fluid on that major surface.

Nonlimiting examples of final substrates can be continuous belts, discrete sheets or parts, cylindrical rolls, spheres, particles, frames, and the like.

The surfaces which the chemically altered first fluid contact can have a variety of surface properties that can alter the physical appearance of the chemically altered first fluid upon contact with the substrate. Nonlimiting
5 examples of the surface properties include porous, microporous, and nonporous surfaces; textured, microreplicated, embossed, or other patterned surfaces; particulate loaded or smooth surfaces; high surface energy or low surface energy surfaces; opaque, clear, translucent, or optically colored surfaces; and radiation
10 sensitive or radiation tolerant surfaces.

In the event that it is preferred that the final substrate not be exposed to the actinic radiation that imposes the conditions that chemically alter the first fluid while in the second fluid, then optionally but preferably, the final substrate can be shielded from the source of actinic radiation without otherwise shielding the
15 first fluid while moving through the second fluid.

The final substrates that are intended for temporary landing spots for the chemically altered first fluid can have any of the above surface properties but preferably have major surfaces with suitable surface energy for providing desired wetting properties of the altered first fluid or facilitated subsequent release.
20 Nonlimiting examples of temporary landing spots include webs that have silicone-containing release surfaces for removal of a liquid that has been polymerized during transport through air, such as the polymerization of liquid monomers to form an adhesive sheet before such sheet contacts a release liner, and a polymeric web with or without a primer to promote wetting and adhesion by a silicone release
25 on a liner.

The final substrates that are intended for permanent sites for the chemically altered first fluid can be any of the final substrates intended for temporary landing spots or can be any other substrate that has any of the above surface properties.

while not adversely affecting the flow of the first fluid through the second fluid. Nonlimiting examples of shields include metal plates, ceramics plates, foam boards, and the like.

5 Post-Delivery Treatment

The delivery of the first fluid in a chemically altered state to the final substrate does not end the possibilities of usefulness of the present invention. Any conventional coating or processing technique of a fluid on a substrate can then be employed to further alter either the physical or chemical properties or both of
10 the first fluid, the substrate, or both.

Nonlimiting examples of post-delivery treatment include embossing, patterning, smoothing, stirring, polymerization, heating, solvent evaporation, calendaring, and the like.

15 Usefulness of the Invention

It has been determined that a particular utility of the present invention is the partially or fully curing of a polymeric material in combination with a carrier fluid coating (as described in Melancon et al. WO 96/23595) or curtain coating which has the advantage of changing the material properties of the
20 formulation in-situ for the purpose of controlling the coating properties.

In particular, a low viscosity, curable formulation can flow freely out of a coating die and then be partially (or fully) cured on a fluid curtain, thereby increasing the viscosity of the formulation that is to be deposited on the substrate.

Another utility of the present invention is the use of this curing
25 method for in-process polymerization of pre-polymers before they contact a heat or light sensitive substrate or multilayer coating, since the substrate itself would receive minimal exposure. Both thermal and radiation cure processes are envisioned in this invention.

The method of this invention could be practiced in combination
30 with the aforementioned Butler et al. invention to generate controlled patterned or porous membranes or films using a fluid carrier coating method.

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A method for chemically altering the composition of a first coating fluid in continuous flow from a dispenser to a final substrate, comprising
5 the steps of:
 - (a) dispensing the fluid in a continuous flow from a source location into a second fluid, and
 - (b) imposing at least one condition on the first fluid to alter the chemical composition of the first fluid before that first fluid leaves the second fluid
10 and contacts the final substrate.
2. The method of Claim 1, wherein the first fluid comprises a liquid, a gas, a combination of liquid and a gas, a combination of two or more gases, a combination of two or more liquids, a supercritical fluid, a combination of
15 a supercritical fluid and a gas, a combination of a supercritical fluid and a liquid, or a combination of two or more supercritical fluids, and wherein the second fluid comprises a liquid, a gas, a combination of liquid and a gas, a combination of two or more gases, a combination of two or more liquids, a supercritical fluid, a combination of a supercritical fluid and a gas, a combination of a supercritical fluid
20 and a liquid, or a combination of two or more supercritical fluids, and wherein the final substrate comprises a solid, at least one liquid on a solid, or at least one gas on a liquid.
3. The method of Claim 1 or 2, wherein the condition imposed
25 comprises a single type of actinic radiation, more than one type of actinic radiation imposed concurrently, or more than one type of actinic radiation imposed sequentially.
4. The method of any of Claims 1-3, wherein the dispenser
30 comprises an extrusion die, a nozzle, a slide die, or other orifice from a source of

the first fluid and wherein the dispensing step comprises curtain coating, carrier fluid coating, extrusion die coating or roll coating.

5 5. The method of any of Claims 1-4, wherein chemical properties of the first fluid are altered during the imposing step in more than one manner.

10 6. The method of any of Claims 1-5, wherein the first fluid comprises a carrier fluid and a functional fluid and wherein the carrier fluid is selected from the group consisting of water, hydrophilic liquids, hydrophobic liquids, noble gases, inert gases, and air, and wherein the functional fluid is selected from the group consisting of monomers, oligomers, pre-polymers, polymers, crosslinking agents, initiators, modifiers, and any other chemical that can exist in fluid form at a single environment of a given temperature, a given pressure, and a given volume and is chemically reactive under any condition during the imposing step.

20 7. The method of Claim 6, wherein the functional fluid further comprises chemical additives, surface active agents, modifiers, particulate fillers, or silicone pre-polymers, and wherein the particulate fillers comprise colloidal silicas.

25 8. The method of Claim 3, wherein each type of actinic radiation comprises infra-red, near infra-red, visible, or ultraviolet light, heat waves, excimer lasers, excimer lamps, electron-beam radiation, microwave radiation, corona-treatment, x-rays, or gamma radiation.

30 9. The method of any of Claims 1-8, wherein the final substrate comprises a continuous belt, a discrete sheet or part, a cylindrical roll, a sphere, a particle, or a frame.

10. The method of Claim 9, wherein the final substrate has surface properties comprising porous, microporous, or nonporous surfaces; textured, microreplicated, embossed, or other patterned surfaces; particulate loaded or smooth surfaces; high surface energy or low surface energy surfaces; opaque, clear, 5 translucent, or optically colored surfaces; or radiation sensitive or radiation tolerant surfaces.

11. The method of Claim 10, wherein the radiation sensitive surface of the final substrate is shielded from the source of actinic radiation without 10 otherwise shielding the first fluid during the imposing step.

12. A coated substrate prepared according to the method of any of Claims 1-11, wherein the substrate has a composition comprising metallic, ceramic, or polymeric materials; naturally occurring or synthetically derived 15 materials; crystalline or non-crystalline materials, or combinations thereof.

INTERNATIONAL SEARCH REPORT

In. tional Application No
PCT/US 97/23509

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B05D3/00 B05D1/00 B05D3/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 970 093 A (SIEVERS ROBERT E ET AL) 13 November 1990 see the whole document	1, 2, 9, 10, 12
X	US 5 464 661 A (LEIN MAUREEN M ET AL) 7 November 1995 see the whole document	1, 2, 9, 10, 12
A	EP 0 506 041 A (UNION CARBIDE CHEM PLASTIC) 30 September 1992 see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Information on patent family members

In. ational Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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